

LIGAND FIELD THEORY OF MAGNETIC ANISOTROPY AND SUSCEPTIBILITY OF Fe^{+2} TUTTON SALTS

B. D. BHATTACHARYYA*

MAGNETISM DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
CALCUTTA-32.

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ABSTRACT. The expression for the magnetic anisotropy and susceptibility of Fe^{2+} Tutton salts have been worked out on the basis of the more general molecular orbital method of Van-Vleck, Stevens and Bose et. al. Both the spin-orbit coupling coefficient and the effective orbital reduction factors along and perpendicular to the tetragonal axis of the complex are reduced anisotropically from their free ion value due to the anisotropic admixture of the central $3d$ -charge cloud with the surrounding s - and p - charge clouds of the ligand oxygen atoms.

INTRODUCTION

A detailed theory of the magnetic anisotropy and susceptibility of Fe^{2+} Tutton salts has been worked out on electrostatic approximations by Bose *et al* (1961). It is found that for the case of $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ the value of the spin orbit coupling is reduced from its free ion value value of -103 cm^{-1} by about 20%, owing to overlap of the central $3d$ charge cloud with the surrounding s - and p - charge clouds of the ligand oxygen atoms. It appears therefore, more reasonable to apply to the problem, the more general method of molecular orbital approximations of Van-Vleck (1932), Stevens (1953) and Bose et. al (1960) so that the correct picture of the energy levels is obtained. It is also reasonable to assume that the overlap is anisotropic, the reduction in the spin-orbit coupling is also taken to be anisotropic in comparing the experimental results on $\text{Fe}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$ of Bose (1948) with our present theory. Since this salt is isomorphous to the ammonium salt (monoclinic, space group $P2_1/a$, 2 mols/cell) and no separate structural data is available, we thus assume for the present purpose, a tetragonal symmetry of the $\text{Fe}^{2+} \cdot 6\text{H}_2\text{O}$ complex as in the other salt (Bose *et. al* 1961).

MOLECULAR ORBITAL THEORY

The five fold orbital degeneracy of the ground state $3d^6 \ ^5D$ of Fe^{2+} ion in the free state, is split up by the predominant cubic component of the crystal field into an orbital doublet E_{2g} and a triplet T_{2g} , the triplet lying lowest.

* Dept. of Physics, St. Xavier's College, Calcutta and honorary research worker, Indian Association for the cultivation of Science, Calcutta-32.

For tetragonal symmetry of the ligand field, the wave functions of the lowest triplet are [Stevens (1953), Bose *et.al* (1961).]

$$\begin{aligned}
 | + > &= -\frac{1}{\sqrt{2}} [|yz> + i|zx>] \\
 | 0 > &= |xy> \quad \dots \quad (1) \\
 | - > &= \frac{1}{\sqrt{2}} [|yz> - i|zx>]
 \end{aligned}$$

where

$$\begin{aligned}
 |yz> &= N[|d, yz> + \lambda\{|p, z, 2> - |p, z, 5> + |p, y, 3> - |p, y, 6>\}] \\
 |xz> &= N[|d, xz> + \lambda\{|p, z, 1> - |p, z, 4> + |p, x, 3> - |p, x, 6>\}] \\
 |xy> &= N[|d, xy> + \lambda\{|p, y, 1> - |p, y, 4> + |p, x, 2> - |p, x, 5>\}] \quad (2)
 \end{aligned}$$

in which N is a normalizing factor and λ is a measure of the amount of mixture of the p -orbits of the ligand oxygen with the central d -orbits of the Fe^{2+} ion.

The appropriate Hamiltonian is

$$\mathbf{H} = \mathcal{H}_{\text{Tetragonal}} + u_z s_z + (u_x s_x + u_y s_y) \quad \dots \quad (3)$$

Since the effective orbital Lande splitting factors $\alpha \simeq \alpha' \simeq 1$ very nearly for a D -state ion.

The effect of the tetragonal field is to split up the above triplet [eqn. (1)] by an amount Δ into a doublet $| + >, | - >$ and a singlet $| 0 >$. It will be seen later in connection with fitting the theory with experimental data, that unless the doublet is taken to lie lowest, no fitting with reasonable values of the parameters is possible.

The spin-orbit interaction takes the form $\Sigma(us)_i$ where u_i i.e. (u_x, u_y, u_z) transform like T_1 octahedral group (Bose *et. al* (1960) then inclusive of covalency, the non-zero matrix elements for u_x, u_y, u_z are given by

$$\begin{aligned}
 <+|u_z|+> &= - <-|u_z|-> = -\zeta_1 \\
 <+|u_x|0> &= <0|u_x|-> = -(\sqrt{2})\zeta_1 \quad \dots \quad (4) \\
 <-|u_y|0> &= <0|u_y|+> = i(\sqrt{2})\zeta_1
 \end{aligned}$$

where ζ_1, ζ_1 are the anisotropically reduced spin-orbit coupling coefficients of Fe^{2+} ion under the ligand field of the complex (Bose *et. al.* 1960). Here z axis is taken along the tetragonal axis of the ion and x, y axes give after orthonormal set with the axis.

Introducing with the five-fold degeneracy of each of the threeorbital states we obtain a secular determinant of the 15th. order which breaks up into two

quadratics, two singlets and a cubic. The eigen values for the $|0\rangle$, $|\pm 2\rangle$ and $|\pm 3\rangle$ states are given as

$$\begin{aligned} E_0 &= \frac{1}{2}[(\zeta_{||} + \Delta) - \{(\zeta_{||} - \Delta)^2 + 24\zeta_{\perp}^2\}^{\frac{1}{2}}] \\ E'_0 &= \frac{1}{2}[(\zeta_{||} + \Delta) + \{(\zeta_{||} - \Delta)^2 + 24\zeta_{\perp}^2\}^{\frac{1}{2}}] \\ E''_0 &= \zeta_{||} \\ E_2 &= \frac{1}{2}[(\Delta - \zeta_{||}) - \{(\Delta + \zeta_{||})^2 + 8\zeta_{\perp}^2\}^{\frac{1}{2}}] \quad \dots (5) \\ E'_2 &= \frac{1}{2}[(\Delta - \zeta_{||}) + \{(\Delta + \zeta_{||})^2 + 8\zeta_{\perp}^2\}^{\frac{1}{2}}] \\ E_3 &= -2\zeta_{||} \end{aligned}$$

and the eigen values for the $|\pm 1\rangle$ states are given by the roots of the cubic

$$x^3 - (2 + \eta)x^2 + (2\eta - 5\rho^2)x + 6\rho^2 = 0 \quad \dots (6)$$

where $x = E_i/\zeta$, E_i being the energy in cm^{-1} , $\eta = \Delta/\zeta_{||}$, $\rho = \zeta_{\perp}/\zeta_{||}$ and $E_i = E_1$, E''_1 and E'_1 respectively;

The corresponding eigenstates are given by

$$\begin{aligned} \psi_1 &= a_1|+, 0\rangle + b_1|0, 1\rangle + c_1|-, 2\rangle \\ \psi_{-1} &= a_1|-, 0\rangle + b_1|0, -1\rangle + c_1|+, -2\rangle \\ \psi_0 &= a_0|+, -1\rangle + b_0|0, 0\rangle + c_0|-, 1\rangle \\ \psi''_0 &= a''_0|+, -1\rangle + b''_0|0, 0\rangle + c''_0|-, 1\rangle \\ \psi''_1 &= a''_1|+, 0\rangle + b''_1|0, 1\rangle + c''_1|-, 2\rangle \\ \psi''_{-1} &= a''_1|-, 0\rangle + b''_1|0, 1\rangle + c''_1|+, -2\rangle \\ \psi_2 &= a_2|+, 1\rangle + b_2|0, 2\rangle \\ \psi_{-2} &= a_2|-, -1\rangle + b_2|0, -2\rangle \\ \psi_3 &= |+, 2\rangle \quad \dots (7) \\ \psi_{-3} &= |-, -2\rangle \\ \psi'_2 &= b_2|+, 1\rangle - a_2|0, 2\rangle \\ \psi'_{-2} &= b_2|-, -1\rangle - a_2|0, -2\rangle \\ \psi'_1 &= \alpha'_1|+, 0\rangle + b'_1|0, 1\rangle + c'_1|-, 2\rangle \\ \psi'_{-1} &= \alpha'_1|-, 0\rangle + b'_1|0, -1\rangle + c'_1|+, -2\rangle \\ \psi'_0 &= a'_0|+, -1\rangle + b'_0|0, 0\rangle + c'_0|-, 1\rangle \end{aligned}$$

where

$$c_1 = \left[\frac{3(2\zeta_{||} - E_1)^2}{2E_1^2} + \frac{(2\zeta_{||} - E_1)^2}{2\zeta_{\perp}^2} + 1 \right]^{-\frac{1}{2}},$$

$$b_1 = \frac{(2\zeta_{||} - E_1)}{(\sqrt{2})\zeta_{\perp}} \cdot c_1$$

and
$$a_1 = - \frac{(\sqrt{3})\zeta_1}{E_1} \cdot b_1$$

For a_1' , b_1' and c_1' we are to replace E_1 by E_1' . Also to get a_1'' , b_1'' and c_1'' we are to replace E_1 by E_1'' .

Further,
$$b_0 = \left[\frac{6\zeta_1^2}{(\zeta_1 - E_0)^2} + 1 \right]^{-1}$$

$$a_0 = c_0 = \frac{(\sqrt{3})\zeta_1}{(\zeta_1 - E_0)} b_0$$

To get a_0' , b_0' we replace E_0 by E_0' and to get a_0'' , b_0'' we must replace E_0 by E_0'' . And finally

$$b_2 = \left[-\frac{2\zeta_1^2}{(\Delta - E_2)^2} + 1 \right]^{-1}$$

$$a_2 = \frac{(\sqrt{2})\zeta_1}{(\Delta - E_2)} b_2$$

Similarly to obtain a_2' , b_2' we replace E_2 by E_2'

3. The g -values

The susceptibility and the g -values are calculated by the usual method of first and second order perturbations with the magnetic field Hamiltonian

$$\mathcal{H} = \beta \cdot (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} \quad \dots \quad (8)$$

The non-zero matrix elements for L being

$$\begin{aligned} \langle + | L_z | + \rangle &= -\langle - | L_z | - \rangle = -k_1 \\ \langle + | L_x | 0 \rangle &= \langle 0 | L_x | - \rangle = -(\sqrt{2})k_1 \\ \langle - | L_y | 0 \rangle &= \langle 0 | L_y | + \rangle = i(\sqrt{2})k_1 \end{aligned}$$

Where k_{11} and k_1 are the orbital reduction factors (Stevens 1953, Bose *et.al* 1960), along and perpendicular to the tetragonal axis of the complex.

Thus we have

$$\begin{aligned} g_{||} &= 2[(c_1^2 - a_1^2)k_{||} + 2b_1^2 + 4c_1^2], \\ g_{\perp} &= 0 \end{aligned}$$

and the principal gm -ionic susceptibilities K_i ($i = ||$ or \perp) are

$$\begin{aligned} K_{||} &= \frac{N\beta^2}{kT} \left[\frac{1}{T} \left\{ G_{1z}E_1 + G_{1z}E_1'' \exp\left(\frac{E_1 - E_1''}{kT}\right) + G_{1z}E_2 \exp\left\{\frac{E_1 - E_2}{kT}\right\} \right. \right. \\ &\quad \left. \left. + G_{1z}E_3 \exp\left(\frac{E_1 - E_3}{kT}\right) + G_{1z}E_3' \exp\left(\frac{E_1 - E_3'}{kT}\right) + G_{1z}E_1' \exp\left(\frac{E_1 - E_1'}{kT}\right) \right\} \right] \end{aligned}$$

$$\begin{aligned}
 & + \left\{ G_{2z} E_1 + G_{2z} E_0 \exp \left(\frac{E_1 - E_0}{kT} \right) + G_{2z} E_0'' \exp \left(\frac{E_1 - E_0''}{kT} \right) \right. \\
 & + G_{2z} E_1'' \exp \left(\frac{E_1 - E_1''}{kT} \right) + G_{2z} E_2 \exp \left(\frac{E_1 - E_2}{kT} \right) + G_{2z} E_2' \exp \left(\frac{E_1 - E_2'}{kT} \right) \\
 & \left. + G_{2z} E_1' \exp \left(\frac{E_1 - E_1'}{kT} \right) + G_{2z} E_0' \exp \left(\frac{E_1 - E_0'}{kT} \right) \right\} \quad \dots \quad (9)
 \end{aligned}$$

where

$$\begin{aligned}
 G_{1z} E_1 &= 2[(4 + k_{11})c_1^2 + 2b_1^2 - k_{11}a_1^2]^2 \\
 G_{1z} E_1'' &= 2[(4 + k_{11})c_1''^2 + 2b_1''^2 - k_{11}a_1''^2]^2 \\
 G_{1z} E_2 &= 2[(2 - k_{11})a_2^2 + 4b_2^2]^2 \\
 G_{1z} E_3 &= 2[4 - k_{11}]^2 \\
 G_{1z} E_1' &= 2[(2 - k_{11})b_2^2 + 4a_2^2]^2 \\
 G_{1z} E_1' &= 2[4 + k_{11})c_1'^2 + 2b_1'^2 - k_{11}a_1'^2]^2 \\
 G_{2z} E_1 &= Y_1^1 + Y_1^2 \\
 G_{2z} E_0 &= Y_0^0 \\
 G_{2z} E_0'' &= Y_0^0 + Y_0^1 \\
 G_{2z} E_1'' &= -Y_1^2 + Y_1^3 \\
 G_{2z} E_2 &= Y_2^2 = G_{2z} E_2' \\
 G_{2z} E_1' &= -Y_1^1 - Y_1^3 \\
 G_{2z} E_0' &= -Y_0^1
 \end{aligned}$$

$$Y_0^0 = \frac{2a_0^2(k_{11} + 2)^2}{E_0'' - E_0}$$

$$Y_0^1 = \frac{2a_0'^2(k_{11} + 2)^2}{E_0' - E_0''}$$

$$Y_1^1 = \frac{2[(4 + k_{11})c_1c_1' + 2b_1b_1' - k_{11}a_1a_1'']^2}{E_1' - E_1}$$

$$Y_1^2 = \frac{2[4 + k_{11})c_1c_1'' + 2b_1b_1'' - k_{11}a_1a_1'']^2}{E_1'' - E_1}$$

$$Y_1^3 = \frac{2[(4 + k_{11})c_1'c_1'' + 2b_1'b_1'' - k_{11}a_1'a_1'']^2}{E_1' - E_1''}$$

$$Y_2^2 = \frac{2(2 + k_{11})^2 a_2^2 b_2^2}{E_2' - E_2}$$

and

$$\begin{aligned}
 K_1 = \frac{2N/\beta^2}{kW} & \left[G_{2x}E_1 + G_{2x}E_0 \exp\left(\frac{E_1 - E_0}{kT}\right) + G_{2x}E_0'' \exp\left(\frac{E_1 - E_0''}{kT}\right) \right. \\
 & + G_{2x}E_1'' \exp\left(\frac{E_1 - E_1''}{kT}\right) + G_{2x}E_2 \exp\left(\frac{E_1 - E_2}{kT}\right) + G_{2x}E_3 \exp\left(\frac{E_1 - E_3}{kT}\right) \\
 & \left. + G_{2x}E_2' \exp\left(\frac{E_1 - E_2'}{kT}\right) + G_{2x}E_1' \exp\left(\frac{E_1 - E_1'}{kT}\right) + G_{2x}E_0' \exp\left(\frac{E_1 - E_0'}{kT}\right) \right] \\
 & \dots \quad (10)
 \end{aligned}$$

where

$$\begin{aligned}
 W = 2 & + \exp\left(\frac{E_1 - E_0}{kT}\right) + \exp\left(\frac{E_1 - E_0''}{kT}\right) + 2 \exp\left(\frac{E_1 - E_1''}{kT}\right) + 2 \exp\left(\frac{E_1 - E_2}{kT}\right) \\
 & + 2 \exp\left(\frac{E_1 - E_3}{kT}\right) + 2 \exp\left(\frac{E_1 - E_2'}{kT}\right) + 2 \exp\left(\frac{E_1 - E_1'}{kT}\right) + \exp\left(\frac{E_1 - E_0'}{kT}\right)
 \end{aligned}$$

and

$$\begin{aligned}
 G_{2x}E_1 &= \frac{2A^2}{E_0 - E_1} + \frac{2A_1^2}{E_0'' - E_1} + \frac{2A_2^2}{E_2 - E_1} + \frac{2A_3^2}{E_2' - E_1} + \frac{2A_{14}^2}{E_0' - E_1} \\
 G_{2x}E_0 &= \frac{2A^2}{E_1 - E_0} + \frac{2A_4^2}{E_1'' - E_0} + \frac{2A_5^2}{E_1' - E_0} \\
 G_{2x}E_0'' &= \frac{2A_1^2}{E_1 - E_0''} + \frac{2A_6^2}{E_1'' - E_0''} + \frac{2A_7^2}{E_1' - E_0''} \\
 G_{2x}E_1'' &= \frac{2A_4^2}{E_0 - E_1''} + \frac{2A_6^2}{E_0'' - E_1''} + \frac{2A_8^2}{E_2 - E_1''} + \frac{2A_9^2}{E_2' - E_1''} + \frac{2A_{15}^2}{E_0' - E_1''} \\
 G_{2x}E_2 &= \frac{2A_2^2}{E_1 - E_2} + \frac{2A_8^2}{E_1'' - E_2} + \frac{2A_{10}^2}{E_3 - E_2} + \frac{2A_{11}^2}{E_1' - E_2} \\
 G_{2x}E_3 &= \frac{2A_{10}^2}{E_2 - E_3} + \frac{2A_{12}^2}{E_2' - E_3} \\
 G_{2x}E_2' &= \frac{2A_3^2}{E_1 - E_2'} + \frac{2A_9^2}{E_1'' - E_2'} + \frac{2A_{12}^2}{E_3 - E_2'} + \frac{2A_{13}^2}{E_1' - E_2'} \\
 G_{2x}E_1' &= \frac{2A_5^2}{E_0 - E_1'} + \frac{2A_7^2}{E_0'' - E_1'} + \frac{2A_{11}^2}{E_2 - E_1'} + \frac{2A_{13}^2}{E_2' - E_1'} + \frac{2A_{16}^2}{E_0' - E_1'} \\
 G_{2x}E_0' &= \frac{2A_{14}^2}{E_1 - E_0'} + \frac{2A_{15}^2}{E_1'' - E_0'} + \frac{2A_{16}^2}{E_1' - E_0'}
 \end{aligned}$$

where

$$A = \sqrt{6}(a_0a_1 + b_0b_1) - \frac{k_{\perp}}{\sqrt{2}} (a_0b_1 + b_0a_1) + 2a_0c_1$$

$$A_1 = \sqrt{6}a_1a_0'' - \frac{k_{\perp}}{\sqrt{2}} b_1 - 2c_1a_0''$$

$$A_2 = \sqrt{6}a_1a_2 - \frac{k_{\perp}}{\sqrt{2}} (a_2b_1 + b_2c_1) + 2b_1b_2$$

$$A_3 = \sqrt{6}a_1b_2 - \frac{k_{\perp}}{\sqrt{2}} (b_1b_2 - a_2c_1) - 2a_2b_1$$

$$A_4 = \sqrt{6}(a_0a_1'' + b_0b_1'') - \frac{k_{\perp}}{\sqrt{2}} (a_0b_1'' + b_0a_0'') + 2a_0c_1''$$

$$A_5 = \sqrt{6}(a_0a_1' + b_0b_1') - \frac{k_{\perp}}{\sqrt{2}} (a_0b_1' + b_0a_1') + 2a_0c_1'$$

$$A_6 = \sqrt{6}a_0''a_1'' - \frac{k_{\perp}}{\sqrt{2}} b_1'' - 2a_0''c_1''$$

$$A_7 = \sqrt{6}a_0''a_1' - \frac{k_{\perp}}{\sqrt{2}} b_1' - 2a_0''c_1'$$

$$A_8 = \sqrt{6}a_1''a_2 - \frac{k_{\perp}}{\sqrt{2}} (b_1''a_2 + b_2c_1'') + 2b_1''b_2$$

$$A_9 = \sqrt{6}a_1''b_2 - \frac{k_{\perp}}{\sqrt{2}} (b_1''b_2 - c_1''a_2) - 2b_1''a_2$$

$$A_{10} = 2a_2 - \frac{k_{\perp}}{\sqrt{2}} b_2$$

$$A_{11} = \sqrt{6}a_1'a_2 - \frac{k_{\perp}}{\sqrt{2}} (a_2b_1' + b_2c_1') + 2b_1'b_2$$

$$A_{12} = 2b_2 + \frac{k_{\perp}}{\sqrt{2}} a_2$$

$$A_{13} = \sqrt{6}a_1b_2 - \frac{k_{\perp}}{\sqrt{2}} (b_1'b_2 - a_2c_1') - 2b_1'a_2$$

$$A_{14} = \sqrt{6}(a_1a_0' + b_1'b_0') - \frac{k_{\perp}}{\sqrt{2}} (a_1b_0' + b_1a_0') + 2c_1a_0'$$

$$A_{15} = \sqrt{6}(a_1''a_0' + b_1''b_0') - \frac{k_{\perp}}{\sqrt{2}} (a_1''b_0' + b_1''a_0') + 2c_1''a_0'$$

$$A_{16} = \sqrt{6}(a_1'a_0' + b_1'b_0') - \frac{k_{\perp}}{\sqrt{2}}(a_1'a_0'b_0' + b_1'a_0') + 2c_1'a_0'$$

It is very reassuring that in the above formidable expressions quite a number of terms are negligible and several others having opposite signs cancel out each other in pairs, so that the final calculations are simplified. Nevertheless we have retained all the terms in the given expressions for the sake of completeness of the theoretical expressions.

EXPERIMENTAL DETAILS

The agreement of the theoretical anisotropy and susceptibility values with the experimental values of Bose (1948) on $\text{Fe}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$ is quite good as can be seen from Table I.

The values of the parameters Δ , ζ_{\parallel} , ζ_{\perp} , k_{\parallel} and k_{\perp} are obtained by trial and error to get the best fit. Our fitting with the experimental results is perfectly unique because even if we try to set the data only at two temperatures we have three unknown parameters Δ , ζ_{\parallel} and ζ_{\perp} whose values can be decided uniquely by fitting with the four observables viz. two mean susceptibilities and two anisotropy values at these two temperatures. However, in view of a large number of earlier experimental findings (Bose (Bose *et al.* 1960, 1961, 1961, 1963, 1964) it is very unlikely that Δ should be constant. If we take temperature variation of Δ into account we can get an unique fitting comparing the experimental results only at three different temperatures because in that case we have altogether five unknown parameters three Δ 's, ζ_{\parallel} and ζ_{\perp} and six observables viz. three mean susceptibility values and three anisotropy values at the three temperatures under consideration.

In the case of $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ the tetragonal field coefficient Δ increases with temperature from a value of 270 cm^{-1} at 20°K to 650 cm^{-1} at 300°K . In the case of $\text{Fe}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$ Δ changes from 240 cm^{-1} at 90°K to 640 cm^{-1} at 300°K . Thus we see that the order of the anisotropic field and also their variations with temperature are almost the same in the two cases.

In the case of $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ the spin-orbit coupling coefficient has been decreased by about 23% from its free ion value of -103 cm^{-1} (Owen 1955, Bose *et al.* 1961). In the case of $\text{Fe}(\text{KSO}_4)_2 \cdot 6\text{H}_2\text{O}$ the spin-orbit coupling coefficients are $\zeta_{\parallel} = -80 \text{ cm}^{-1}$, $\zeta_{\perp} = -88 \text{ cm}^{-1}$ instead of the free ion value of -103 cm^{-1} . This indicates again almost the same overlap between the $3d \text{ Fe}^{2+}$ and s - and p - O^{2-} charge clouds, except that the overlap here has been taken as anisotropic.

If the tetragonal field coefficient Δ is negative, we have a singlet lying lowest after the tetragonal field and after introducing the spin-orbit coupling one magnetic singlet comes lowest with a doublet close to it. In this case K_{\perp} becomes greater than K_{\parallel} whereas when Δ is positive we have a doublet ($m = \pm 1$) lying lowest,

K_{11} is necessarily greater than K_{\perp} . For the assumption that $K_{\perp} > K_{11}$ i.e., for Δ negative we could not fit the susceptibility and anisotropy both simultaneously for any reasonable values of the parameters. Hence we fit with our experimental results considering Δ to be positive.

In the case of $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ we have for $\Delta = 270 \text{ cm}^{-1}$ $g_{11} = 8.989$, $g_{11} = 0$. In the case of the potassium salt $g_{11} = 8.48$, $g_{\perp} + 1 = 0$, $\Delta = 240 \text{ cm}^{-1}$ which appear to agree well with the g -values given by Tinkham (1956) for FeF_2 in ZnF_2 at 20°K . Since the crystalline field in FeF_2 has been found to be truly orthorhombic and also must be appreciably different in magnitude from that in Tutton salts owing to the difference in structure, the agreement is perhaps fortuitous, but nevertheless indicates that the order of magnitudes are comparable within the limits of approximation involved.

TABLE I

Fe(KSO ₄) ₂ · 6H ₂ O		k_{\parallel} = 0.95	ζ_{\parallel} = -80 cm ⁻¹
		k_{\perp} = 0.80	ζ_{\perp} = -88 cm ⁻¹
tempr °K	cm^{-1}	p^2	$p^2 - p_{\perp}^2$
			g -values
300°K	640	28.57	10.31
		(28.58)	(10.34)
220°K	416	28.13	12.87
		(28.08)	(12.70)
90°K	240	26.00	22.10
		(26.27)	(22.01)
$g_{\parallel} = 8.48$			
(8.989)			
$g_{\perp} = 0$			
(0)			

The values in the parenthesis in the 3rd. and 4th. column give the experimental results of Bose (1948). The g -values within parenthesis in the 5th. column are Tinkham's (1956) on FeF_2 diluted with ZnF_2 which have been discussed above.

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